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㉕ Composition and process for the preservation of wood.

㉖ Composition for the preservation of wood containing a wood preservative, such as a boron compound or a fluorine compound, in a polymer or polymer composition, which upon contact with water releases the wood preservative. Said composition is introduced into a hole in the wood or in a wood construction, whereafter the hole is sealed.

**EP 0 152 976 A2**

Composition and process for the preservation of wood.

The invention relates to a composition and a process for the preservation of wood.

5        It is generally known that wood may be preserved by impregnating it, where appropriate under reduced pressure, with solutions, emulsions or suspensions which contain wood preservatives. Disadvantages of this method of preservation are that in most cases much more preservative is used than is effectively  
10        needed for the preservation, since it is desired to compensate for losses by leaching-out and evaporation and since the preservative is also introduced into parts of the wood where it is not directly necessary, that it is often troublesome to introduce the preservatives into the wood, that the preservatives, as regards their toxicity,  
15        are often dangerous to those who carry out the wood preservation treatment and that burning of wood thus treated can result in pollution of the environment.

      These disadvantages are also encountered with the process of the German Patent Specification 1,299,848, according to which a  
20        mixture of 35-50 % by weight of boric acid and 65-50 % by weight of ammoniumbifluoride is used as a wood preservative, as well as with the process of the Swiss Patent Specification 306,709, according to which an aqueous solution of bifluorides, such as a mixture of potassium bifluoride and ammoniumbifluoride, is applied on the wood  
25        and care is taken that the gases formed in the wood cannot escape therefrom, e.g. by coating the wood with a water-soluble synthetic resin.

      Consequently, many attempts have been made to overcome these disadvantages. Thus, according to Netherlands Patent Application  
30        77,03412 wood preservatives have been introduced only locally into the wood by applying a wood preservative in liquid or paste-like form into a hole made in the wood and thereafter tightly sealing the hole. In this way, a source of the wood preservative is introduced into the wood and continuously releases the preservative. If,  
35        for example, the preservative is taken up in a solvent which evaporates slowly impregnation of the wood takes place gradually around the hole. A disadvantage of this method is, however, that

penetration of the preservative into the wood also occurs where this is not necessary because no moisture is present and thus fungi are not active. Consequently, after a relatively short time the preservative has become fixed in the wood over a limited distance, for example 5-8 cm, around the point of introduction. When using commercial products on this basis, in the form of capsules containing, for example, tributyltin oxide in an organic solvent, which capsules are introduced into the hole and thereafter crushed by introducing a dowel, the capsules then releasing their contents to the surrounding zone, it is necessary to work very carefully and to ensure that the skin and clothing do not become contaminated with the content of the capsules when the latter are broken.

Further, Netherlands Patent Application 78,10841 discloses a process wherein fused bodies are introduced into drill holes in the wood, which bodies contain a wood preservative which is solid at ambient temperature. Boron trioxide is mentioned as an example of such an agent. In addition to boron trioxide, other metal oxides may also be present, these serving to control the rate of solution of the boron trioxide in water or to increase the preservative action. Suitable materials are, for example, oxides of alkali metals, which increase the rate of solution, oxides of alkaline earth metals or silicon, which reduce the rate of solution, or copper, tin or zinc oxides, which boost the preservative action of the boron trioxide. The fused body is in the shape of a rod, block or ball which fits into the drill hole which has been made. Disadvantages of this process are that boron trioxide is a relatively expensive substance and that a high concentration of boron trioxide in certain positions is disadvantageous in that it causes boron trioxide to strike through a coat of paint applied to the wood.

The same disadvantages are encountered with the use of a wood preserving tablet comprising a mixture containing at least two boron compounds selected from any two of the three groups of boron compounds namely (a) borates, (b) boric acids and (c) boric oxides as disclosed in U.K. Patent Application 2,114,003.

It is the object of the invention to overcome the disadvantage of the known compositions and processes and to develop compositions which when used in certain positions in the wood and wood con-

structions result in long-lasting preservation, with release of wood preservative taking place only in positions where this is necessary, and when this is really necessary.

5 It has been found that these objectives are achieved with compositions which contain the wood preservatives in a polymer or polymer composition which on coming into contact with water releases the wood preservative. This polymer or this polymer composition containing the wood preservative is introduced into the wood or the wood construction.

10 When such compositions have been introduced into the wood, the actual wood preservatives enter the wood only when the latter becomes damp, in other words when there is a danger of rotting. When the wood remains dry, the preservative does not penetrate into it. The preservative thus remains available for longer than is the case  
15 in the processes hitherto used. Moreover, as a result of the very gradual release of the wood preservative and the lower local concentration thereof than was possible hitherto, strike-through of the agent through paint coats is not to be expected.

20 Polymers or polymer compositions which are suitable for the compositions according to the invention are water-soluble and water-swellaable polymers or polymer compositions. The water-soluble polymers include, for example, water-soluble polyvinylpyrrolidone, polyvinyl alcohol, polyethylene glycol and polyacrylamide.

25 Water-swellaable polymers or polymer compositions are particularly suitable, for example the so-called polymer alloys which are known from Netherlands Patent Application 79,08799. These are polymer alloys which are stable at up to high temperatures, are homogeneous, and are prepared from component (a) one or more high molecular polymers possessing anhydride groups and component (b)  
30 one or more high molecular polymers containing groups which can interact with hydrogen atoms, in which alloy the components (a) and (b) are bonded to one another via a hydrogen bridge through complete or partial protolysis of component (a). In general, components (a) and (b) each have a molecular weight of at least 10,000.  
35 Component (a) consists, for example, of one or more high molecular copolymers of a monomer with alkene unsaturation, preferably styrene and maleic anhydride, and component (b) of polymers possessing

ester groups, for example polyvinyl acetate, a copolymer of ethylene and vinyl acetate, a polyacrylate, a polymethacrylate or cellulose esters. These polymers can be prepared, for example, by first preparing a solution of component (a) in an organic solvent, to which solution there is then added component (b), with the component (a) present in solution being completely or partially protolysed under the action of protolysing agents, before or after the addition of component (b), after which the solvent is removed. Examples of particularly useful polymer alloys are copolymers of styrene and maleic anhydride together with polyvinyl acetate in weight ratio's of 10:90 to 70:30, for example 25:75 to 60:40, and especially of 30:70 to 50:50.

However, other polymers or copolymers which conform to the requirement that only upon contact with water do they release the active wood preservative may also be used.

The mechanism which comes into action when using the compositions for the preservation of wood can be explained as follows with reference to the polymer alloy known from Netherlands Patent Application 79,08799. Upon contact with water, the polymer alloys swell and the wood preservative contained in the polymer alloy is released to the surroundings. The swelling is reversible. When the polymer alloy is no longer in contact with water, the swelling and hence the release of the active agent diminishes. Both the speed of swelling and the degree of swelling influence the rate of release of the wood preservative and the release thereof can thus be regulated. Moreover, the rate of release depends on the shape and size of the particles which are introduced into the wood or the wood construction. The composition is mostly used in the form of pellets, granules, tablets, cylindrical shapes and the like.

When the polymer or polymer composition in the hole in the wood is swelling upon contact with moisture, it is pressed against the wall of the hole. Thereby the transfer of active substance from the composition in the hole to the surrounding wood is promoted.

For the accurate control of the release of the wood preservative it may be desirable to coat the polymer or the polymer composition, containing the wood preservative, with a water permeable coating, thereby retarding the release of the wood preservative

from the actual composition. Possible materials for the coating are polymers having satisfactory water permeability. For example, water soluble or water-swellable polymers of polymer compositions, such as are employed for the actual compositions containing the wood preservative, may be used for the coating. The coating may for example be applied by dipping the polymer or the polymer composition, containing the wood preservative, in a coating solution consisting of a polymer or a polymer composition in an organic solvent, such as acetone, butan-1-one, or butan-2-one. The concentration of the polymer or the polymer composition in this solution is, for example, 10-30 % by weight, generally around 20 % by weight. By varying the polymer or polymer composition of the coating and the polymer or polymer composition containing the wood preservative the most desirable rate of release of the wood preservative employed can be found experimentally. The thickness of the coating also plays a role.

As wood preservative it is in principle possible, to use, in the composition and in the process according to the invention, all wood preservatives suitable for this purpose. However, it has been found that boron compounds and fluorine compounds are especially satisfactory. Furthermore, quaternary ammonium compounds appeared to be suitable.

Boron compounds have a long-lasting action and good results are obtained with a mixture of borax and boric acid, for example the commercial product Basilit B (Bayer AG, Leverkusen, Federal Republic of Germany), which product contains 15.2 % by weight of boron.

In the compositions according to the invention, fluorine is in general present in the form of a bifluoride. When a composition containing fluorine comes into contact with water in the wood, hydrogen fluoride is formed and this migrates very rapidly through the wood. In practice, the fluorine-containing wood preservative used is, for example, the commercial product Improsol, which contains 42.5 % by weight of  $\text{KHF}_2$ , 52.5 % by weight of  $\text{NH}_4\text{HF}_2$  and 5 % by weight of a wetting agent and which is marketed by Holz-Verf B.V. in Enschede.

Boron and fluorine compounds are less toxic to the user than



the tin compounds hitherto extensively used, such as tributyl-tin oxide, or organic chlorine compounds, such as pentachlorophenol. Since polymers or polymer compositions which in the dry state have a very low diffusion coefficient for the wood preservative are used for the pellets, granules and similar shaped articles, there is little to be feared from touching the shaped pieces when introducing them into the wood. However, as soon as the composition comes into contact with moisture in the wood, it releases its wood preservative, which then performs its function, that is to say destroys the harmful micro-organisms.

Very good results have been obtained with wood preservative compositions of the invention containing both a boron compound and a fluorine compound as wood preservatives. These compounds appear to be compatible. It also appears that it is possible to control the release rate of the active compounds by variation in the composition of the polymer or polymer composition and/or of the coating.

The compositions according to the invention can inter alia be used with very good results to preserve deal, which per se does not keep very well but which is troublesome to impregnate. Also with oak good results have been obtained.

It should be noted that in the wood preservative composition according to the invention the wood preservative can be incorporated into the polymer or polymer composition together with fillers, such as saw dust, or with other additives.

Per se, it was known to incorporate preservatives in polymers. Thus, Netherlands Patent Application 77,03306 discloses a process for the preparation of non-fouling paints, in particular for ships, wherein, in one stage of the process of preparation, solid toxic substances, for example organo-tin compounds, are added in the form of granules, scales or pieces, which consist of a matrix of one or more polymeric paint binders containing finely dispersed toxic substance particles, optionally complemented with other materials customary in the paints industry. The granules, scales or pieces of polymer matrix and toxic substance can be dissolved in a paint solvent, using a simple mixing apparatus, and thus give a non-fouling paint. However, the polymers used for this purpose absorb very

little or no water and upon contact with water only release the toxic substance extremely slowly. Hence, they are unsuitable for use in the preservation of wood, where rapid release of wood preservative upon contact with water is necessary.

5 Further, it is known from Netherlands Patent Application 77,03305 to prepare paint compositions which consist of a combination of one or more water-insoluble polymeric binders, one or more  
10 water-soluble polymeric binders and one or more sparingly water-soluble solid toxic substances, optionally complemented with other materials customary in the paint industry, the ratio of the components being so chosen that upon painting surfaces normally exposed to water the paint coat obtained, upon exposure to the surface  
15 water during navigation abrades in such a way that just sufficient toxic substance is released to prevent fouling of the painted article. During the abrasion, the water-soluble component is dissolved and the integrity of the outermost layer is destroyed. The latter releases the toxic substance contained therein, after which the same takes place with the layer directly beneath the outermost layer. The compositions according to the present invention are unusable for this known application. Soluble polymers or polymer compositions present in the compositions according to the present invention will, upon contact with water, rapidly and completely disintegrate therein, while water-swella-  
20 ble polymers or polymer compositions will release the toxic substance much too rapidly though, in contrast to the combinations of polymers used according to Patent Application 77,03305, they will not lose their integrity. For use in preserving wood, on the other hand, the combinations of polymers according to Patent Application 77,03305 cannot be used since, in the preservation of wood, no abrasion or shear forces  
25 occur.

30 Further, it is known from Netherlands Patent Application 69,11410 to use synthetic high molecular polymers as carriers in granules which contain substances having a biological, in particular pesticidal, action. However, in this literature reference no  
35 mention is made of the use of the granules for preserving wood, and equally there is no mention of a polymer or polymeric composition which in the presence of water releases wood preservative and/or

forms a hydrogel which only in this condition of a hydrogel slowly releases wood preservatives contained in the composition.

Finally it is known from Bull.Chem.Soc.Jpn 56, 2177-2178 (1983) to react the fungicidal compound o-phenylphenol with acryloylchloride and to subject the resulting 2-biphenylylacrylate to homopolymerization or to copolymerization with vinylacetate, styrene or N-vinylpyrrolidone. When the polymer or copolymer obtained was subjected to hydrolysis at pH 6 and 8, it appeared that the o-phenylphenol was released gradually from the molecule of the polymer or copolymer to which it was anchored. However, in the compositions of the invention the wood preservative is not anchored to the molecule of the polymer or polymer composition.

The examples which follow illustrate the invention without imposing a limitation thereon.

#### Example I

This example describes the preparation of a number of compositions which contain boron in the form of the preparation Basilit B, a mixture of borax and boric acid having a boron content of 15.2 % by weight. The polymers used for the compositions were polymer alloys obtained according to Netherlands Patent Application 79,08799.

The following compositions were prepared:

#### Composition B1

Small sheets of size 45x80x1 mm were compression-moulded from granules of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of polyvinyl acetate, at a temperature of 155°C and under a pressure of 3432 kPa for 5 minutes. These sheets were dipped in an aqueous solution of 15 % by weight of Basilit B at a temperature of 70°C. After 3 hours, maximum swelling had been reached, after which the sheets were dried in a forced stream of air at 50°C. The weight increase was 50.7 %. This corresponds to a Basilit B content of 33.6 % by weight.

#### Composition B2

Composition B1 was immersed in a 20 % by weight solution, in butan-2-one, of a polymer alloy consisting of 10 % by weight of

copolymer of styrene and maleic anhydride and 90 % by weight of polyvinyl acetate. After it had been dried in a forced stream of air at 50°C, the composition obtained was again immersed in a 20 % by weight solution of the said polymer alloy in butan-2-one. The composition was again dried in a forced stream of air at 50°C. The thickness of the coating with the polymer alloy of 10 % by weight of a copolymer of styrene and maleic anhydride in 90 % by weight of polyvinyl acetate was 160-170  $\mu\text{m}$ .

Composition B3

Using the method described for composition B2, composition B1 was twice immersed in a 20 % by weight solution, in butan-2-one, of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of an ethylene/vinyl acetate copolymer, and was then dried.

Composition B4

Using the method described for composition B1, small sheets were produced from a polymer alloy consisting of 50 % by weight of a copolymer of styrene and maleic anhydride and 50 % by weight of polyvinyl acetate. 40.5 % by weight of Basilit B is introduced therein by impregnation.

Composition B5

Composition B4 was coated by immersion with a 20 % by weight solution in butan-2-one of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of a copolymer of ethylene and vinyl acetate, in the manner described for composition B3.

Composition B6

A powder mixture consisting of 33 % by weight of Basilit B and 67 % by weight of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of polyvinyl acetate was prepared. This mixture was first compression-moulded for 15 minutes at 155°C and thereafter ground and subsequently again compression-moulded for 15 minutes at 190°C to give sheets of 1 mm. These sheets melted during the second pressing and were relatively clear and homogeneous.

Composition B7

Small sheets of 2 mm thickness were produced in the manner

described for composition B6.

Composition B8

Small sheets were produced, in the manner described for composition B6, from a powder mixture consisting of 50 % by weight of Basilit B and 50 % by weight of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of polyvinyl acetate.

Composition B9

10 % by weight of triacetin were added, by atomising, to a mixture of 50 % by weight of ground easily swellable foam of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of polyvinyl acetate, and 50 % by weight of Basilit B. Homogeneous small sheets were obtained by sinter-pressing at room temperature and subsequent pressing at 160°C for 15 minutes.

Composition B10

Using the method described for composition B9, a mixture of 50 % by weight of ground Basilit B and a pulverulant polymer alloy consisting of 50 % by weight of a copolymer of styrene and maleic anhydride and 50 % by weight of polyvinylacetate was compression-moulded to give small sheets.

Composition B11

Basilit B powder was compression-moulded at 190°C to give small sheets. These sheets were coated, in the same manner as that described for composition B2, with a 20 % by weight solution, in butan-2-one, of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of an ethylene/vinyl acetate polymer.

Composition B12

30 Basilit B powder was compression-moulded at 190°C to give small sheets. These sheets were coated, in the manner described for composition B2, with a 20 % by weight solution, in butan-2-one, of a polymer alloy consisting of 10 % by weight of a copolymer of styrene and maleic anhydride and 90 % by weight of polyvinyl acetate.

35 The sheets, thus obtained, of compositions B1 to B12 inclusive were introduced into a polyethylene bottle containing 150 ml of distilled water. The bottle plus contents was carefully shaken at

room temperature by means of a shaking machine which had a travel of 10 cm and a frequency of 20 oscillations per minute. A sample of 10 mlitre was dried after 30 minutes, 2 hours, 8 hours and 30 hours respectively. This sample was subsequently diluted 50-fold and analysed for boron. From the results obtained, the half-life was determined, that is to say the time at which half of the originally present boron had been released from the polymer matrix. These half-lives are shown in Table A below.

10

TABLE A

Half-lives (t) for the release of boron from  
compositions B1 to B12 inclusive

Composition	t(min)	Composition	t(min)
B1	10	B7	1060
B2	1200	B8	10
B3	960	B9	10
B4	20	B10	10
B5	850	B11	420
B6	90	B12	280

20

Table A shows that the compositions B1, B4, B9 and B10 exhibit a rapid release of boron because of the hydrophilic effect of these compositions and moreover because of the fragmentation during shaking. At the same time, composition B4 also becomes gel-like. The coating has a marked effect on the release of boron. Thus the half-life of the two compositions B2 and B3 was found to be much greater than that of the uncoated composition B1. Moreover, a coating with a polymer alloy consisting of 10 % by weight of a copolymer of styrene and maleic anhydride and 90 % by weight of polyvinyl acetate was found to lead to a slower release of boron than a coating obtained with a polymer alloy of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of an ethylene/vinyl acetate copolymer. Furthermore, the mechanical properties of the first-mentioned coating were found to be better than those of the last-mentioned coating this being clear from the flaking-off of the last-mentioned coating during the test concerning the release of boron. In the case of the coated small

35

5 sheets of pure Basilit B (composition B11 and B12), the situation is somewhat similar. Here again, the release from samples having the last-mentioned coating was found to occur more rapidly than from sheets having the first-mentioned coating. Finally, however, it is also found that the uncoated sheets dissolved completely within 2 minutes while the coated sheets had a considerable half-life (compositions B11 and B12). From the fact that composition B8 showed a substantially lower half-life than composition B6 it can be concluded that part of the Basilit B present in composition B8 is not dissolved in the polymer matrix.

#### Example II

15 A number of compositions were prepared with the aid of the preparation Improsol which consists of 42.5 % by weight of potassium bifluoride, 52.5 % by weight of ammonium bifluoride and 5 % by weight of wetting agent. A 10 % by weight solution of this preparation in water has a pH of 3.8. The fluoride content of the dry substance is 56 % by weight.

20 The polymers used for compositions F2 to F8 inclusive were polymer alloys obtained according to Netherlands Patent Application 79,08799.

#### Composition F1

25 A solution of 5.0 g of polyvinylpyrrolidone in 15 ml of distilled water was mixed with a solution of 5 g of Improsol in 15 ml of distilled water. The mixture was carefully evaporated to dryness under reduced pressure at 40°C, to give a final weight of 9.525 g. The weight loss was due to evolution of hydrogen fluoride. Pills of the mixture obtained were produced by pressing.

#### Composition F2

30 Compositions F1 was immersed in a 10 % by weight solution, in butan-2-one, of a polymer alloy consisting of 10 % by weight of a copolymer of styrene and maleic anhydride and 90 % by weight of polyvinyl acetate, in such a way that after removing the solvent the weight of the pills showed an increase of 21 %.

#### Composition F3

35 Composition F1 was immersed in a 10 % by weight solution of a polymer alloy consisting of 30 % by weight of a copolymer of sty-

rene and maleic anhydride and 70 % by weight of an ethylene/vinyl acetate polymer, in such a way that after removing the solvent the weight of the pills showed an increase of 20 %.

#### Compositions F4

5        Soxleth tubes produced from cellulose fibres and having sizes of 11x28 mm<sup>2</sup> and 9x40 mm<sup>2</sup> were used as the reservoir for Improsol. The length of the tubes was so chosen that the thinner tube was completely filled with 300 mg of Improsol. The wider tube was pushed over the filled thin tube and the sealing join was smeared  
10       full with a suspension of cellulose fibres.

#### Composition F5

Tubes according to composition F4 were impregnated with a 10 % by weight solution, in butan-2-one, of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride  
15       and 70 % by weight of an ethylene/vinyl acetate copolymer, by pouring the butanone solution into the tubes, then again rapidly removing the solution and thereafter allowing the tubes to drain and to dry. The weight increase was 15 %.

#### Composition F6

20       The Soxleth tubes with composition F4 are impregnated in the manner described for composition F5, with a 10 % by weight solution, in butan-2-one, of a polymer alloy consisting of 10 % by weight of a copolymer of styrene and maleic anhydride and 90 % by weight of polyvinyl acetate. The weight increase was 16 %.

#### Composition F7

25       15 g of easily swellable foam of a polymer alloy consisting of 30 % by weight of a copolymer of styrene and maleic anhydride and 70 % by weight of polyvinyl acetate (particle size 0.5-1 mm) were thoroughly mixed, on a roller stand, with 15 g of Improsol  
30       (particle size 0.3-0.7 mm). Small sheets of thickness 2 mm were compression-moulded from this mixture at room temperature.

#### Composition F8

The small sheets of composition F7 were coated with a 10 % by weight solution, in butan-2-one, of a polymer alloy consisting of  
35       10 % by weight of a copolymer of styrene and maleic anhydride and 90 % by weight of polyvinyl acetate. The weight increase was 12 %.

The pills and tubes containing Improsol were introduced into a



polyethylene bottle containing 100 ml of distilled water and shaken carefully at room temperature by means of the shaking machine described in Example I. At regular intervals of time, a sample of 1 ml was taken and mixed with 20 ml of a mixture of equal amounts by weight of distilled water and a buffer. The content of fluoride ions in the solution obtained was determined electrometrically. From the results obtained, the half-life, that is to say the time at which half of the originally present fluorine had been released from the polymer matrix, was determined. These half-lives are shown in table B below.

TABLE B  
Half-lives (t) of release of fluorine from compositions F1 to F8  
inclusive

Composition	t(min)
F1	16
F2	35
F3	8
F4	25
F5	38
F6	140
F7	18
F8	17

A comparison of Table B with Table A shows that the release of the fluorine compound in general takes place much more rapidly than the release of boron. In both cases, a coating with a polymer alloy consisting of 10 % by weight of a copolymer of styrene and maleic anhydride and 90 % by weight of polyvinyl acetate is found to delay the release most.

#### Example III

In the manner described in Example I and Example II a number of compositions were prepared, which contained both Basilit B and Improsol. The formulation of these compositions is shown in table C. The half-lives for the release of boron and of fluorine from said compositions were determined in the manner described in

Example I and Example II respectively. The results of these measurements are shown in table D. By way of comparison compositions B4 and F7 were examined once again.

TABLE C

Composition	Constituents of composition % by weight				Coating constituents (proportions)	thickness $\mu\text{m}$
	Basillit B	Improsol	PSMA/PVAC (50/50)	PSMA/PVAC (30/70)		
B4	40	0	60	0	no coating	
F7	0	45	0	55	no coating	
C1	23	25	27	25	no coating	
C2	23	25	27	25	PMVMA/PVAC (50/50)	50
C3	23	25	27	25	PSMA/PVAC (30/70)	20
C4	23	25	27	25	PSMA/PVAC/PVAL (30/35/35)	50
C5	23	25	27	25	PSMA/PVAC (30/70)	50
C6	23	25	27	25	PSMA/PVAC (30/70)	50
C7	31	33	36	0	stearyl aminated PMVMA/PVAC (50/50)	50

## Legenda of Table C.

PSMA = copolymer of styrene and maleic anhydride

PVAC = polyvinylacetate

5 PMVMA = copolymer of methylvinylether and maleic anhydride

PVAL = copolymer of vinylacetate and vinylaurate (80/20)

(For PSMA/PVAC (50/50) vide composition B4 in Example I)

(For PSMA/PVAC (30/70) vide composition F7 in Example II)

10

TABLE D

Half-lives (t, hours) for the release of boron and fluorine from  
compositions B4, F7 and C1 to C7 inclusive

15

Composition	boron	fluorine
B4	0.33	-
F7	-	0.35
C1	1.3	1.0
20 C2	5.5	3.6
C3	9	8.3
C4	17	23.5
C5	21	38
C6	28	55
25 C7	2.3	1.5

Example IV

Preservation tests were carried out with composition B4 from  
Example I and composition F7 from Example II. From composition B4,  
30 cylinders with a height of 30 mm and a diameter of 11.8 mm, thus  
having a volume of 3338 mm<sup>3</sup>, were produced. From composition F7,  
cylinders with a height of 30 mm and a diameter of 12.0 mm, thus  
having a volume of 3394 mm<sup>3</sup>, were produced.

100 test blocks of the wood variety Picea abies (deal) were  
35 produced. The dimensions were 40x70x300 mm (end-face surface 40x70  
mm). The angle which the year rings made with the sides of the end  
faces was 45°.

A hole 50 mm deep was drilled in the centre of the 40x300 mm surface. In the case of the 50 blocks intended for composition B4 the diameter was 12.5 mm and in the case of the 50 blocks which were intended for composition F7 the diameter was 13.0 mm.

5        4 similar holes with a diameter of 3.2 mm and a depth of 17 mm were drilled at 20 and 50 mm distance of the centre of the above-mentioned drill holes. An insulated brass nail was hammered into each hole. The nails served, in pairs as measurement points for the determination of the moisture content in the test blocks during the  
10       test.

The appropriate compositions were introduced into the blocks after which the holes were sealed with a beechwood dowel of height 20 mm and diameter 12.5 or 13 mm respectively.

Each series of 50 blocks was divided into two groups of 25  
15       blocks, namely two groups per composition. One group per composition was kept at a relative humidity (RH) of 90 % at room temperature while the blocks of the other group were placed with one end face on the bottom of glass pots. Thereafter, sufficient demineralised water was introduced into the pots for about 75 mm of  
20       the blocks to stand under water.

The moisture content of the test blocks was determined before starting the test and after 1, 2, 4, 8 and 12 weeks. For this, an electrical moisture meter from Siemens was used. The brass nails served as the measurement points.

25       After 2, 4, 8, and 12 weeks 5 blocks from each group of 25 blocks were dried for 3 days at room temperature. Thereafter they were sawn through in the lengthwise direction parallel to the 70x300 mm surface. On the sawn surface of one of the two halves obtained from each block, the active substance concerned was colour-  
30       revealed by means of a suitable reagent.

The degree of diffusion was determined by measuring the surface of the coloured zones by means of a planimeter. In the case of the blocks taken out of water, the coloured zones on the water side and the air side were measured separately.

35       The colour reagents used for boron were a solution of 240 mg of curcumin in 200 ml of ethanol and a solution of 12.0 g of salicylic acid in 40 ml of concentrated hydrochloric acid and 60 ml of

ethanol. The sawn surface was succesively sprayed with these solutions. If boron was present, a purplish red colour resulted. The colour reagents used for fluorine were a solution of 840 mg of alizarin in 99.2 ml of water and a solution of 840 mg of zirconium chloride in 40 ml of 25 % by weight hydrochloric acid and 59.2 ml of water. The sawn surface was sprayed with a mixture of the two solutions in a ratio of 1:1. If fluorine was present, a yellow colour resulted.

The results of the moisture measurements are shown in Tables E and F and the results of the measurements of the coloured surface areas are shown in Tables G and H.

TABLE E

Moisture contents in percent of blocks of deal. Mean of 5 measurement results.  
 Measurement point A : 20 mm from the centre of the borehole  
 Measurement point B : 50 mm from the centre of the borehole  
 Composition: B4

Conditions	Start		After 1 week		After 2 weeks		After 4 weeks		After 8 weeks		After 12 weeks	
	A	B	A	B	A	B	A	B	A	B	A	B
90 % relative humidity	9.2	9.5	11.5	11.6	16.2	16.9	18.2	18.0	18.0	18.0	20.3	20.1
Above water	9.6	9.5	14.4	16.4	17.8	21.4	22.0	28	23.0	>28	>28	>28

TABLE F

Moisture contents in percent of blocks of deal. Mean of 5 measurement results.

Measurement point A : 20 mm from the centre of the borehole

Measurement point B : 50 mm from the centre of the borehole

Composition: F7

Conditions	Start		After 1 week		After 2 weeks		After 4 weeks		After 8 weeks		After 12 weeks	
	A	B	A	B	A	B	A	B	A	B	A	B
90 % relative humidity	9.8	9.7	12.4	11.4	19.2	16.3	24.6	18.2	> 28	26.5	> 28	> 28
Above water	9.8	9.8	14.4	16.1	23.1	21.2	26.0	> 28	> 28	> 28	> 28	> 28



TABLE C

Diffusion surface areas in  $\text{cm}^2$  and in percent of the cross-sectional surface area of the test block ( $\approx 210 \text{ cm}^2$ )  
Composition: B4

	90 % relative humidity			Above water		
	After 2 weeks	After 4 weeks	After 8 weeks	After 12 weeks	After 2 weeks	After 4 weeks
Diffusion surface area in $\text{cm}^2$	13.0	11.74)	15.0	19.6	1)	6.1
					2)	6.6
					3)	12.7
						13.5
						22.6
						36.0
Diffusion surface area in percent of the cross-sectional area of the test block	6.0	5.54)	7.1	9.3	1)	2.9
					2)	3.1
					3)	6.0
						6.3
						10.7
						17.0

- 1) water side
- 2) air side
- 3) total

4) Since the colour reactions were carried out at different intervals of time on different blocks, variations in the results must be expected. The relatively low values after 4 weeks are ascribed to this.

TABLE H

Diffusion surface areas in  $\text{cm}^2$  and in percent of the cross-sectional surface area of the test block ( $\approx 210 \text{ cm}^2$ )  
Composition: F4

	90 % relative humidity						Above water					
	After		After		After		After		After		After	
	2 weeks	4 weeks	8 weeks	12 weeks	2 weeks	4 weeks	8 weeks	12 weeks	2 weeks	4 weeks	8 weeks	12 weeks
Diffusion surface area in $\text{cm}^2$	51.4	78.7	92.1	111.8	1)	30.1	51.1	59.2	59.7			
					2)	28.5	43.4	50.0	54.0			
					3)	58.6	94.5	109.2	113.7			
Diffusion surface area in percent of the cross-sectional area of the test block	24.4	37.4	43.8	53.2	1)	14.3	24.3	28.2	28.4			
					2)	13.5	20.6	23.8	25.7			
					3)	27.8	44.9	52.0	54.1			

- 1) water side
- 2) air side
- 3) total

It may be seen from Tables G and H that for roughly the same moisture content the diffusion surface area within a given period is much greater when using fluorine than when using boron.

Example V

In the manner described in Example IV for composition F7 experiments with said composition were carried out with 8 blocks of oak. 4 blocks were kept at a relative humidity of 90 % at room temperature, 4 other blocks being placed with one end face on the bottom of glass pots, into which demineralised water was introduced.

The moisture content after 1 week, 2 weeks and 12 weeks as well as the degree of diffusion after 12 weeks were determined as described in Example IV for composition F7.

The results are shown in tables K and L.

TABLE K

Moisture contents in percent of blocks of oak. Mean of 4 measurement results.  
 Measurement point A : 20 mm from the centre of the borehole  
 Measurement point B : 50 mm from the centre of the borehole  
 Composition: P7

Conditions	Start		After 1 week		After 2 weeks		After 12 weeks	
	A	B	A	B	A	B	A	B
90 % relative humidity	15.2	15.5	18.5	19.1	22.0	20.6	25.0	21.7
Above water	15.8	15.8	18.6	19.6	20.2	21.0	20.7	21.0

TABLE L

Diffusion surface area in  $\text{cm}^2$  and in percent of the cross-sectional surface area of the test block (=  $210 \text{ cm}^2$ )

Mean of 4 measurement results

Composition: F7

	90 % relative humidity	Above water
	After 12 weeks	After 12 weeks
Diffusion surface area in $\text{cm}^2$	96	69
Diffusion surface area in percent of the cross-sectional area of the test block	46	33

C L A I M S

1. Composition for the preservation of wood, which composition contains a wood preservative in a polymer or polymer composition which upon contact with water releases the wood preservative.
2. Composition according to claim 1, characterised in that the polymer or polymer composition is swellable in water.
3. Composition according to claim 2, characterised in that the polymer composition is a polymer alloy prepared from component (a) one or more high molecular polymers possessing anhydride groups and component (b) one or more high molecular polymers containing groups which can interact with hydrogen atoms, in which alloy the components (a) and (b) are bonded to one another via a hydrogen bridge through complete or partial protolysis of component (a).
4. Composition according to claim 3, characterised in that the polymer alloy consists of (a) a copolymer of styrene and maleic anhydride and (b) polyvinylacetate or a copolymer of ethylene and vinyl acetate.
5. Composition according to claim 1, characterised in that the polymer or polymer composition is water-soluble.
6. Composition according to claim 5, characterised in that the polymer consists of polyvinylpyrrolidone.
7. Composition according to claims 1 to 6, characterised in that the polymer or the polymer composition, containing the wood preservative, is coated with a water-permeable coating.
8. Composition according to claim 7, characterised in that the coating consists of a water-permeable polymer or a water-permeable polymer composition.
9. Composition according to claim 7 or 8, characterised in that the coating consists of a polymer or polymer composition which is water-soluble or water-swellable.
10. Composition according to claims 1 to 9, characterised in that the wood preservative contains one or more boron compounds.
11. Composition according to claim 10, characterised in that the wood preservative is boric acid and/or borax.
12. Composition according to claim 11, characterised in that the wood preservative is a mixture of boric acid and borax.

13. Composition according to claims 1 to 9, characterised in that the wood preservative contains a fluorine compound.
14. Composition according to claim 13, characterised in that the wood preservative is a mixture of potassium bifluoride and ammonium bifluoride.
- 5 15. Composition according to one or more of the preceding claims, characterised in that the composition contains both a boron compound and a fluorine compound as wood preservatives.
16. Composition according to one or more of the preceding claims, characterised in that the composition is in the form of a pellet, a
- 10 pill or a cylinder.
17. Process for the preservation of wood, characterised in that a composition according to one or more of the preceding claims is introduced into a hole in the wood or in a wood construction, and
- 15 the hole is sealed.
18. Wood or wood construction possessing, in a sealed space within the wood or the wood construction, a composition according to one or more of claims 1 to 16.

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